

Synthesis of bulk amorphous and nano-crystalline materials by spray forming

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Abstract

Bulk amorphous and nanocrystalline metallic materials have been observed to possess excellent mechanical and physical properties. The conventional process routes to synthesize such materials are restricted by their ability to achieve rapid solidification which limits the dimensions of the materials produced. In the last ten years, spray forming has been used to avoid these limitations by using its layer by layer deposition of undercooled droplets. The available literature indicates that the opportunities provided by this process can be utilized to produce bulk materials in a single step. In the present paper, an attempt has been made to review the developments in the area of spray forming of amorphous and/or nanocrystalline materials. The effect of process parameters, droplet size distribution in the spray, the thermal conditions of droplets prior to deposition and the deposition surface conditions have been discussed in detail. It has been demonstrated that the layer by layer deposition of undercooled droplets of glass forming alloys on a relatively cold deposition surface is the suitable condition to achieve amorphization/nanocrystallization. A critical analysis of the process parameters and the results has been made based on the composition, glass forming ability and possible mechanisms of microstructural evolution.

Keywords: spray forming, amorphous, nanocrystalline, undercooling.

1.0 Introduction

Bulk amorphous and nanocrystalline metallic materials have been of considerable interest for the last 30 years due to their exceptional physical and mechanical properties. The mechanical properties of bulk metallic glasses (BMGs) show a unique combination of high strength, 1 GPa in the case of Mg-based BMGs and 3–4 GPa in the case of Fe or Co-based

BMGs, and low Young's modulus (80–90 GPa), together with an elastic strain of around 2%, which is much higher than that of common crystalline metallic alloys (<1%) [Par93, Joh99, He04, Lof03, Ino04, Ino00]. A large number of glass forming metallic alloy compositions have already been explored and developed e.g. Zr-, Cu-, Ti-, Pd-, La-, Fe-, Mg- and Al-based alloys. For most of the alloys compositions, a high cooling rate of the liquid becomes the principal parameter during solidification, to avoid crystallization, that lead to sluggish kinetics. In general, the cooling rates needed for avoiding crystallization varies with the alloys system being vitrified and depends upon the glass forming ability (GFA) of that particular composition. Some of the compositions (such Pd- and Zr- based systems), having high GFA, can be vitrified even at cooling rates of $1\text{--}100\text{ Ks}^{-1}$ [Ino98, Wan04] but a complete vitrification of other alloys require a high cooling rate of the order of $10^3\text{--}10^6\text{ Ks}^{-1}$ [Li09, Ino90, Per02]. The requirement of such a high cooling rate for poor glass formers limits at least one of the dimensions of the solidifying material to so small a value, which can vary from a few hundred microns to a few millimeters, that a high surface area to volume ratio is achieved. Therefore, several techniques have been evolved to achieve such high cooling rates to synthesize amorphous materials e.g. melt spinning, gas atomization, and copper mold casting etc. Melt spun ribbons or gas atomized powders thus produced are not directly applicable to mass utilization unless these are consolidated in bulk. Bulk production of amorphous/nano-crystalline materials using melt spun ribbons or gas atomized powders as primary raw material has been successfully attempted and the product has demonstrated their edge over the conventionally produced materials [Sen05, Li03, Wan08, Kaw01, Kim04, Sor03]. However, the large number of process steps and the possibility of contamination during powder handling involved in the consolidation of amorphous powders or ribbons are the limitation for industrially viable production process. In addition, the glassy systems being thermodynamically metastable with respect to the crystalline state cannot be heated at elevated temperatures, during consolidation, for long duration without running the risk of inducing crystallization of the amorphous phase [Kim04]. These characteristics severely limit the consolidation parameters that can be used for bulk synthesis.

Basing our understanding on the above processes a revisit at the rapid solidification processing routes indicate that a high undercooling, achieved due to high cooling rate and thereby leading to kinetic arrest, is the prime requirement for the amorphization of the alloy melt [Ino98, Per02]. A little consideration of the amorphization process would indicate that a process consisting of a discontinuous generation of highly undercooled melt droplets and their layer by layer deposition on a substrate might result in the formation of dense and consolidated bulk materials. The well known spray forming process is one of such techniques where this kind of rapid solidification effect and layer by layer deposition is possible. In the last two decade, a number of investigations have been carried out on spray forming of glass forming alloys and their subsequent characterization. It has been demonstrated in these studies, as listed in the Table 1, that spray forming can be a potential technique to produce

partially amorphous and/or nano-crystalline materials. However, the progress in this direction has not been so effective; and this may be due to the fact that spray forming is already a matured process and the different studies till date do not demonstrate consistently encouraging outcomes in terms of amorphous phase fraction. Secondly, due to the skeptical views on the industrial processing and applicability of such materials, efforts in this direction are restricted to a few laboratories only.

Therefore, the present paper is an attempt to review the researches carried out on the development of amorphous or nano-crystalline materials by spray forming. The aim of the paper is to bring out the consolidated efforts made and results obtained by various investigators; and to critically analyze the achievements so far. A perspective approach for further possibilities and the future prospects would be brought out.

2.0 Spray forming process

As spray forming is already a well established process [Lav96, Gra95, Sri04, Lav92, Gra07, Sri07, Sri05, Sri08, Sri01a, Sri01b], we attempt to introduce the process briefly and discuss only those aspects of the process which has direct relevance to the present subject i.e. producing amorphous or nano-crystalline materials. Spray forming consists of two distinct but integral processes of gas atomization of a melt into a spray of droplets and its subsequent deposition onto a substrate. The gas atomization of melt produces a wide size range of droplets which experience high cooling rate depending upon their size that determines the specific surface area. However, the degree of undercooling is also influenced by the presence of any potential catalytic nucleants in the melt which may come due to impurities. During disintegration of the melt stream the total number of potential nucleation sites is divided into various droplets leaving large fraction of droplets free of nucleants, particularly when the mean droplet size is small, thereby increasing the possibility of high undercooling in the nucleant free droplets. The fraction of nucleant free droplets increases with decrease in the droplet size [Shu01, Sri09a]. Therefore, to achieve high undercooling, either the melt purity has to be high or the droplet sizes need to be small. The second aspect of the spray is the wide size range of droplets. This leads to different degrees of undercooling for variously sized droplets. To achieve uniformity in the microstructure the spread of droplet sizes need to be small [Sri09a]. This depends upon the nozzle design and process parameters used for the atomization. A narrow size distribution of droplets ensures similar cooling conditions for a large fraction of droplets. A typical example of the various microstructural features of differently sized droplets is shown in fig. 1a for $\text{Al}_{85}\text{Y}_8\text{Ni}_5\text{Co}_2$ system. This reveals partially crystalline, fully crystalline and featureless or amorphous/nanocrystalline particles. Figure 1b shows two particles of similar sizes, where one is fully crystalline with obvious coarse primary phase and the other depicts primary phase in an optically featureless nano-crystalline or amorphous phase. The SEM picture in fig. 1c is the back scattered electron image showing

particles with coarse primary crystals, small secondary crystals and featureless surfaces. It is obvious from the structure in fig. 1d that even when primary crystallization commences the remaining undercooled liquid may be kinetically arrested and further crystallization or growth would be restricted. The spray condition, which is generally used for the deposition of non-glass forming alloys to get pore-free, dense and refined microstructural feature may not be suitable for the synthesis of uniform amorphous/nanocrystalline phases.

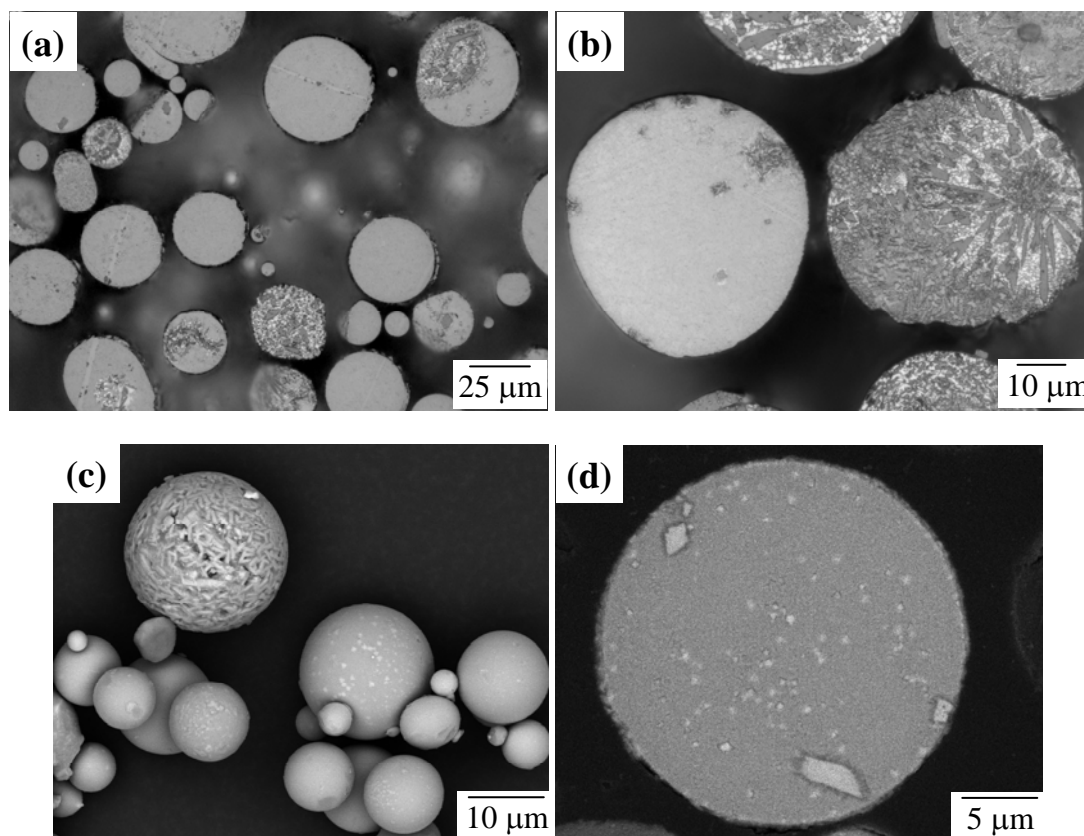


Fig. 1: (a-b) optical micrographs of gas atomized $\text{Al}_{85}\text{Y}_8\text{Ni}_5\text{Co}_2$ powders (25-50 μm) showing large fraction of featureless particles along with particles having various other structural features (c) SEM back scattered image (BSI) revealing different features even for similar sized particles (d) BSI of cross section of a particle depicting large primary phase and small secondary crystals in an amorphous/nanocrystalline matrix [Sri10].

In the recent years, several studies have been reported that pertain to the development of amorphous materials by spray forming. The alloy systems studied by various investigators are Al-, Fe-, La- and Mg-based alloys, see Table 1. It has been observed in most of the cases that only partial amorphization of deposit can be achieved. As the deposit thickness increased the material, in the top layers in particular, showed only crystalline phases. However, in some cases, fully amorphous phase could be achieved. In the next section, therefore, the details of these studies have been brought out and have been discussed in terms of composition, deposit size, phases evolved and parameters used.

3.0 Studies on amorphization / nanocrystallization by spray forming

3.1 Al-based systems

The first report on the development of amorphous materials by spray deposition was published by Oguchi et al. in the year 1990 [Ogu91, Ogu90], to the best of authors' knowledge, on $\text{Al}_{84}\text{Ni}_{10}\text{Mn}_6$ system. In this experiment (fig. 2), a high pressure gas atomization process was used to atomise the melt at 9.8 MPa pressure and the deposition was done on a rotating copper substrate, with the diameter of 250 mm and a minimum speed of 4000 rpm. A fully amorphous sheet of 7 mm was produced with characteristics similar to melt spun ribbons of the same composition. This showed the efficacy of the two stage liquid quenching technique.

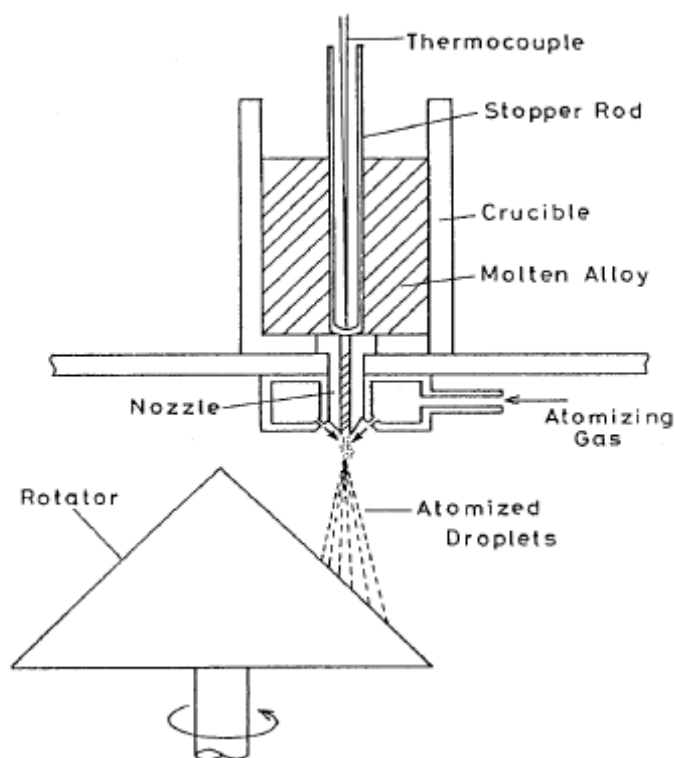


Figure 2: An illustration of a two stage quenching equipment with high pressure gas atomization and rotating Cr coated copper cone [Ogu90, Ogu91]

After a gap of ten years from the above study, Afonso et al. [Afo01a, Afo01b] attempted spray forming of $\text{Al}_{85}\text{Y}_8\text{Ni}_5\text{Co}_2$ and $\text{Al}_{84}\text{Y}_3\text{Ni}_8\text{Co}_4\text{Zr}_1$ systems using a high gas to melt (G/M) mass flow ratio of 10 and 8.7 m^3/kg , respectively. A high volume fraction of 76% amorphous phase, calculated based on the total heat of crystallization compared to fully amorphous melt spun ribbons, has been reported for AlYNiCo system. The AlYNiCoZr system showed fully crystalline billet. However, the oversprayed powders in this case contained 40% amorphous phase fraction. The presence of amorphous phase in AlYNiCo produced at high G/M was attributed to the impact of a high volume fraction of solid amorphous and nanostructures

particles having low heat content which did not allow reheating of the billet above the recrystallization temperature. Guo et al. [Guo05, Guo07] reported amorphous phase fraction of 36% in spray formed $\text{Al}_{89}\text{La}_6\text{Ni}_5$ sheet of 2-3 mm thickness. In this study, a number of nanocrystalline intermetallic phases were also observed along with some unknown phases. In one of the similar experiment, Guo et al. [Guo06] produced 30 mm thick billet of $\text{Al}_{85}\text{Nd}_5\text{Ni}_{10}$ and found that the billet was fully crystalline. However, the oversprayed powder showed 63% of amorphous phase fraction. A liquid nitrogen cooled copper substrate was used so as to engender fast cooling of the deposit during and after deposition. Srivastava et al. [Sri09b, Sri10] used $\text{Al}_{85}\text{Y}_8\text{Ni}_5\text{Co}_2$ for spray forming using commercial purity elements. However, in contrast to the other investigators, who attempted cooling the substrate using liquid nitrogen, a heated substrate was used in this study to make 12 mm thick plate having width of 250 mm and length of 600 mm. The substrate in these experiments was 30 mm thick copper. This led to 83% and 56% amorphous phase in the bottom and top regions of the plate. It was observed in these studies that the solidification sequence of the droplets before and after deposition had considerable effect on the final deposit microstructure. In a recent work, Zhuo et al. [Zhuo11] showed 91.7%, 78% and 54.3% amorphous phase fraction in the bottom, middle and top of a 12 mm thick plate, respectively, for $\text{Al}_{86}\text{Si}_{0.5}\text{Ni}_{4.06}\text{Co}_{2.94}\text{Y}_6\text{La}_{0.5}$ system atomized with argon gas at 0.6 MPa. Similarly, Yan et al. [Yan11], in their attempt to get amorphous powders of the $\text{Al}_{86}\text{Ni}_6\text{Y}_{4.5}\text{Co}_2\text{La}_{1.5}$ system, concluded that in such compositions the first phase to form was Al_2Y instead of fcc-Al, and this is the leading crystalline phase during solidification followed by precipitation of Al. In all the above studies, the powders and deposits showed nanocrystalline structure along with some fraction of coarse primary intermetallic phases and amorphous phase. It is clear from the above experiments (summarized in Table 1) that the composition and process parameters affect the amorphous phase fraction in the material.

3.2 Fe-based systems

Saito et al. [Sai98] reported in the year 1998 fully amorphous phase, with limited amount of $\text{Fe}_{14}\text{Nd}_2\text{B}$ intermetallic phase, in 3 mm thick spray deposited $\text{Fe}_{77}\text{Nd}_{15}\text{B}_8$ system. Spray forming in this study was accomplished using a high pressure of 6.0 MPa and a nozzle diameter of 2 mm. In contrast to the deposit, the oversprayed powders showed fully crystalline state. It was concluded in this study that the cooling rate of the deposit was higher than that obtained during gas atomization. This is possibly due to the two stage cooling of droplets. Afonso et al. [Afo04] attempted the $\text{Fe}_{83}\text{Zr}_{3.5}\text{Nb}_{3.5}\text{B}_9\text{Cu}_1$ system by spray forming and found fully crystalline deposit with large fraction of intermetallic phases. In this experiment, a low gas pressure of 1.0 MPa, nozzle diameter of 6 mm and a superheat of 300 °C were employed. Low pressure and large nozzle diameter may have led to large size droplets, high superheat may lead to high heat content prior to deposition and a larger nozzle diameter will increase the liquid flow rate thus slow cooling and larger droplet size. All these parameters are not

favourable for a high cooling rate, and also engender a high heat transfer to the deposit. In a recent publication, Catto et al. [Cat11] reported 95% amorphous phase, up to 4 mm of a 16 mm thick deposit, in $[(\text{Fe}_{0.6}\text{Co}_{0.4})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ system. In this experiment also, parameters were similar to that used by Afonso et al. [Afo04], however, the deposit showed considerable fraction of amorphous phase. This again emphasizes that the composition plays an important role during synthesis of amorphous phase. Secondly, amorphous phase formation only up to 4 mm of the deposit indicates that the incoming droplets do not get enough quenching so as to transform to an amorphous phase during subsequent deposition of droplets. This is ascribed to the heat accumulation in the deposit as the thickness increases.

3.3 Mg-based systems

The amorphous materials based on Mg show high specific stiffness; and a critical cooling rate of 100 K/s has been observed for Mg-Cu-Y system. Replacing Y with Gd results in better GFA and up to 8 mm diameter amorphous material can be synthesized for $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ by copper mold casting [Xi04, Men03, Yua05]. Chang et al. [Cha08] attempted spray forming of $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ and produced 12 mm thick deposit, using a nozzle diameter of 6 mm and gas to melt flow ratio of 2.4 m³/kg on a 5 mm thick copper substrate. This led to the formation of amorphous phase in the bottom (0-2 mm) but fully crystalline structure in the top region (7-12 mm). The question arises as to why the spray forming route did not result in larger fraction of amorphous structure even when the glass forming ability of this system is high enough for large diameter copper mold casting.

4. Process stages

An understanding of the overall spray deposition process and the affect the different cooling stages is necessary to develop an insight into how suitable process parameters for the production of bulk metallic glasses differ from those generally employed for the production of crystalline materials. Spray forming is mostly divided in the droplet cooling and the deposit cooling phase with cooling rates of 10^3 - 10^4 K/s and 10^0 - 10^1 K/s, respectively [Gra07, Fri04, Ber04, Gra95]. However, a novel division in three sub-processes [Mey12], namely droplets in flight, droplets on deposition and post deposition cooling is discussed here.

4.1 Droplets in flight

In spray forming, different atomization techniques can be used to disintegrate the melt into individual droplets. Most common are free-fall [Gra95, Mey12, Ach10, Ell10] and close-coupled atomizers [Gra95, Kas07, Kas04], but also other atomizers have already been used in spray forming processes [Ell04, Hug08, Che98, Ach07]. The aim of atomization is to increase

the surface-to-volume-ratio of the melt. During their flight phase, the droplets release heat due to convection and radiation to their ambient [Fri04, Ber00, Wis02]. The major influencing parameter, that not only influences the surface-to-volume-ratio of the droplets but also the convective heat transfer coefficient [Fri04, Ber00, Ell07], is the droplet diameter.

In summary, to achieve high cooling rates, an atomization technique that produces small droplets such as close-coupled-atomization is favored.

4.2 Droplets on deposition

This second stage is the transition from a spray of liquid, semi-solid or solid droplets to the deposit which has to be considered carefully. When a droplet impacts and spreads on the substrate or deposit surface, it releases heat mainly by conduction to the deposit [Don07] during and after the spreading phase until it reaches an equilibrium state [Mey12]. For the smallest droplet fractions in the spray, it is also possible that they have a lower thermal energy than the deposit surface and that they would reheat to the equilibrium state [Gra07]. The conductive heat transfer between the droplet and the surface depends on their temperature difference as well as the thermal contact resistance between them. Both are dependent on the first and third cooling stage that determines the thermal state of the droplet and the surface. The thermal contact resistance is determined by how the droplet spreads: if the surface is too cold, too much heat from the droplet is released and the solidifying droplet cannot spread uniformly [Abe06, Dhi05, Dhi07]. This can then lead to an irregular contact surface and hence to an increased contact resistance not only for this, but also for the following droplets [Gha04]. This phenomenon is well known in spray forming when cold substrates are used and a porous layer in the substrate vicinity forms [Uhl07, War97]. If a high heat transfer between the deposit and the substrate is necessary, too cold surface conditions of the substrate and the deposit should be avoided.

It was shown previously [Sri10] that the average amorphous fraction of overspray powder is lower than that found in the deposits, which indicates that the cooling rate during deposition and subsequent cooling of deposit must be higher than that during droplet cooling. As post-deposition cooling is known to slow, the droplet deposition stage must be a key cooling process for the production of bulk metallic glasses by spray forming.

4.3 Post deposition cooling

When a splat reaches its thermal equilibrium with the surrounding splats or deposit surface, it enters the post deposition cooling stage. Simplifying, this stage can also be understood as a layer-wise growth process due to its timescale in the order of seconds [Mey12, Ach10]. The cooling rate in the deposit is determined by a balance of incoming and outgoing heat flows: heat is transferred into the deposit by new layers being deposited while heat can be released by

surface convection and radiation as well as by conduction to the substrate. If less heat is released than introduced into the deposit from the spray, an accumulation of heat will take place and lead to critical conditions for the production of bulk metallic glasses, where a continuous, fast cooling is needed. As the third cooling stage is most critical because of its low cooling rate, process conditions that affect this stage should be chosen carefully.

The convective heat transfer to the ambient is given by the difference of deposit surface temperature and the ambient temperature, the convective heat transfer coefficient and the deposit surface area. Usually, the surface and ambient temperature cannot be influenced so strongly that it would lead to a drastic change of convective heat transfer. The heat transfer coefficient is given by the flow situation, especially the nozzle type used and the deposit geometry. A change of the atomization gas flow rate also leads only to a moderate change of the heat transfer coefficient [Fri04, Mey03]. To achieve a strong cooling effect, a change of the deposit geometry to increase the surface area - for example a doubling of the diameter of a spray formed tube - is suited to achieve a strong effect. It should be noted that this effect is limited by the coverage of the gas flow from the atomizer: if only a small part of the deposit is covered, the remaining part releases heat only due to natural convection, so that the overall effect is low. In summary, the main parameter to change the convective heat transfer is the change of the deposit surface area. This can also be done by choosing a different type of deposit, such as a flat product instead of a billet. Same considerations are valid for the heat release by radiation.

Conductive heat transfer to the substrate becomes important, when the thermal resistance between deposit and substrate are low and when the substrate has enough heat capacity to take up a large amount of heat from the deposit before both reach equilibrium. Copper is usually a suited material because of its high density and specific heat as well as high thermal diffusivity. Thick substrates are preferable so that the equilibrium temperature of the substrate and the deposit will be below the glass forming temperature. It is important to pre-heat the substrate to achieve a low thermal resistance between the deposit and substrate and hence a high heat transfer. This becomes more crucial as the deposit thickness increases and hence more heat has to be conducted through the first layers into the substrate.

At this point, heat will not only be released conductively to the substrate and by convection and radiation to the ambient, but also more heat from impacting droplets will be transferred into the deposit. It is important to not to introduce more heat into the deposit than being released to allow a continuous cooling of the deposit. If this is the case and the heat release cannot be increased further, the incoming heat flow needs to be reduced. This can either be achieved by adjusting the parameters of cooling stage (i.e. by reducing the particle diameter) or, if this is not possible, by reducing the deposit growth rate and hence increasing the growth time of a certain layer thickness and therefore it has time to release heat. It was shown by calculations [Mey12] that the mass flow is a key parameter to influence the thermal history of a deposit. Using a pyrometer to measure its surface temperature gives the opportunity to

actually control reliably the thermal state of the deposit during and after deposition. However, commonly used free-fall and close-coupled-atomizers usually cannot be run with the low mass flows required, so that there is a need for the implementation of alternative atomizers, such as pressure-gas-atomization or impulse atomization, for the spray forming process.

5.0 Mechanism of microstructural evolution

As discussed above, the mechanism of microstructural evolution during spray deposition of glass forming alloys can be said to be governed in three stages (1) in-flight droplet cooling (2) cooling and solidification on deposition and (3) post deposition cooling. In the following sections, attempt has been made to critically analyze all these cooling stages and find out a qualitative correlation between cooling and the microstructural features.

5.1 Microstructure constitution of the spray

In general, an undercooled droplet solidifies in a sequence as given in column 'A' of fig. 3. The primary crystallization takes place, latent heat is released and solidification continues till a solid particle is formed. It is depicted in the figure that a droplet has different solidification states during the course of its flight i.e. different solid fraction. A very small sized droplet may experience such a high cooling rate that the crystallization is fully avoided. The undercooling of the droplet may also change the solidification sequence such that the formation of primary phase is avoided and small secondary crystals are formed, as shown in figure 1d. Very fine droplets may solidify amorphous without giving way to crystallization. However, in the case of a glass forming alloy the viscosity of the liquid increases as the temperature of the liquid decreases, and therefore the diffusion of elements in an undercooled multi-component glass forming system becomes tedious. In such a case, the heat transfer as well as atomic transfer from the interface of primary phase becomes difficult. On the other hand, rapid heat extraction from the droplets surface continues. This may result in solidification of the droplet where primary crystals do not grow due to high viscosity of the undercooled liquid around and the liquid solidifies either as nano-crystalline or amorphous state, as depicted in figure 1b. Therefore, the spray usually contains semi-solid droplet (with varying solid fraction and microstructural constituents depending upon the cooling rate of the droplet), undercooled droplets, fully crystalline particles and amorphous particles. Such a wide range of droplet's solidification states eventually leads to a highly inhomogenous structure of deposit. However, a narrow size distribution of droplets can be expected to ensure uniformity in the solidification state, as a large fraction of droplets would be in a narrow size range, which is a strong factor in determining the cooling rate of droplets.

5.2 The transient layer on deposition

The aim of the present article is to see how an amorphous or nanocrystalline bulk deposit can be produced by spray forming. Therefore, droplets in the spray which have already witnessed crystallization are of little importance and the effort should be made to achieve the droplet deposition in undercooled state containing minimum heat.

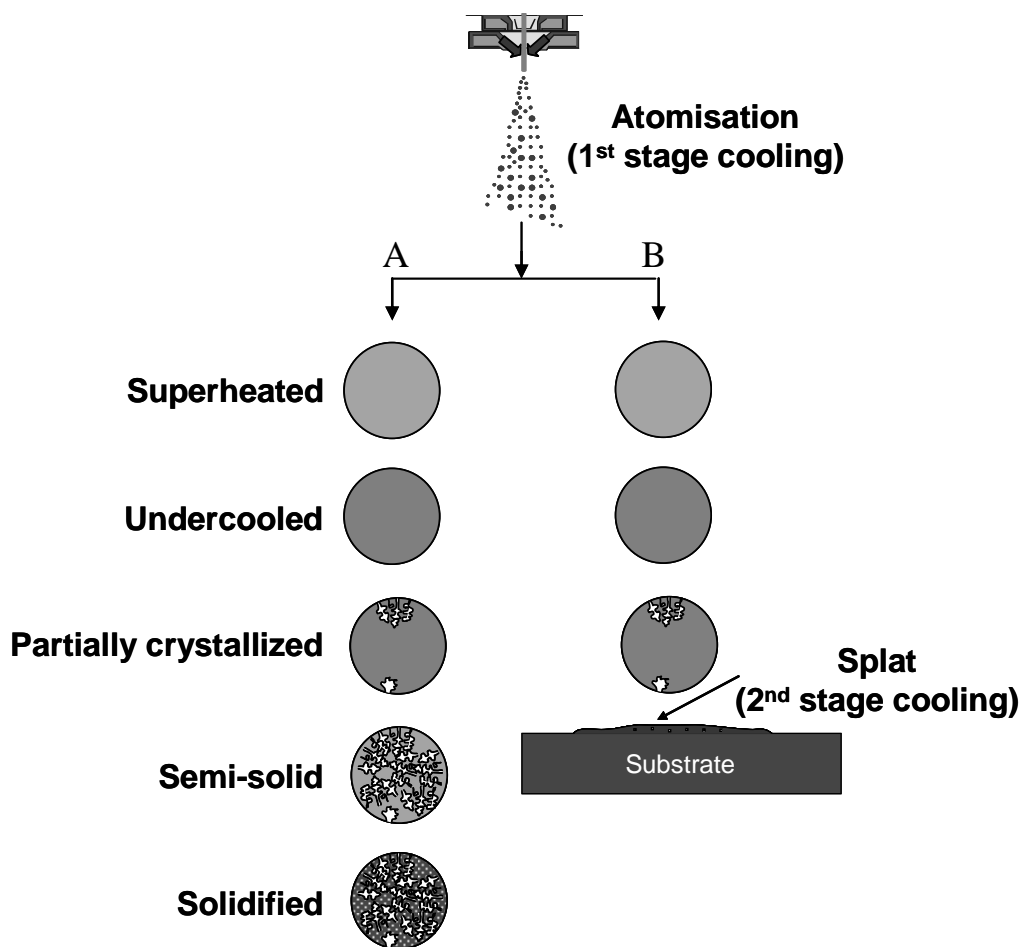


Figure 3: A schematic showing that a liquid drop which crystallizes at a given cooling condition can give rise to higher fraction of amorphous or nanocrystalline structure when cooled in the 2nd stage.

Fig. 4 shows a schematic path of cooling of a liquid droplet. The time axis is indicative of the flight distance of the droplet in the spray. The pictures on the right indicate the possible structural features achieved in these cooling/solidification conditions. A slowly cooled droplet in the spray undercools and finally crystallizes and become fully crystalline, if there is no hindrance in the droplet's trajectory. However, a droplet with high cooling rate may cross the glass transition temperature without witnessing the crystallization event. If a moderately undercooled droplet, which generally experiences slow cooling, is to be brought to the glassy

state a high cooling rate is required. This can be obtained by splating it on a relatively cold surface/substrate, say at point A (beginning of the 2nd cooling stage, as shown in fig. 3 column 'B').

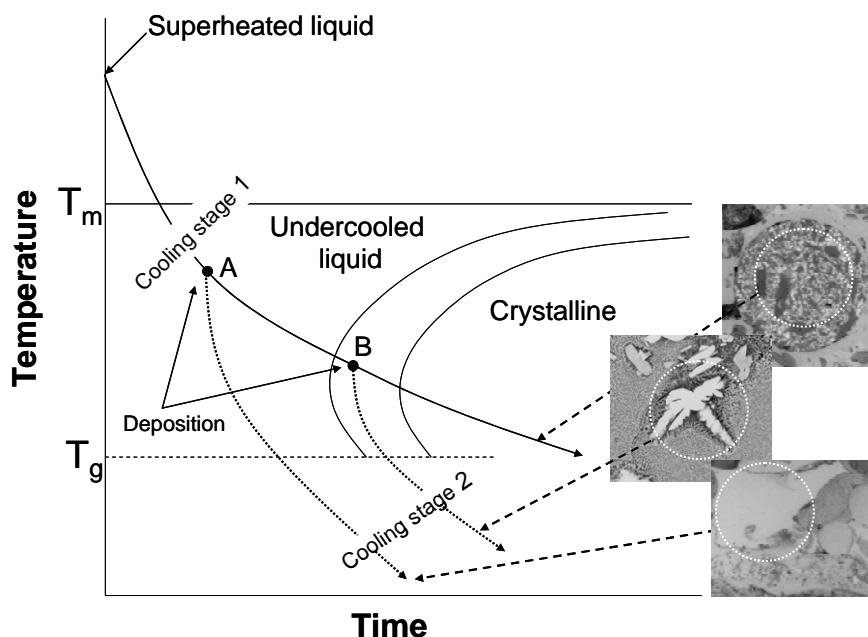


Figure 4: Different stages of cooling for undercooled or partially crystallized liquid drops. Second stage cooling of undercooled drops can directly engender amorphous phase, whereas, partially crystallized drops may lead to a mixture of crystalline and amorphous phase. Amorphous phase formation is due to the quenching of remaining undercooled liquid.

However, the time (or flight distance) at which the droplet splats the surface governs the total heat content transferred to the substrate. A deferred impact of the droplet ensures low heat content, as some of the heat will be extracted by the gas jet during flight, but high possibility of the droplet being crystallized. A high heat content transfer to the substrate, as the layer of droplet's spray keep on impinging one over the other, may be detrimental to the already amorphized droplets by leading to crystallization. On the other hand, if the crystallization commences and the droplet enters the two phase region (point B in fig. 4), a large fraction of droplet will be in undercooled state. If the droplet impinges the substrate in this state (say point B), the undercooled liquid will immediately solidify amorphous along with already crystallized primary phase. The effect of this phenomenon can be seen in fig. 5. The figure shows a deposited droplet where crystallization commenced and large size primary phase formed, growing radially from the nucleation region. The grey region 'A' signifies the area where the effect of the release of latent heat could be sensed by the system and small secondary crystallization was evidenced. However, the area far away from the nucleation regions did not witness crystallization and solidified in undercooled state leading to nanocrystallization and/or amorphization. Fig. 6a shows the as cast structure of an Al-Y-Ni-Co based system depicting large size primary intermetallic phases in an eutectic matrix. In

contrast, almost featureless regions, which are optically irresolvable, can be observed in the spray formed deposit (fig. 6b).

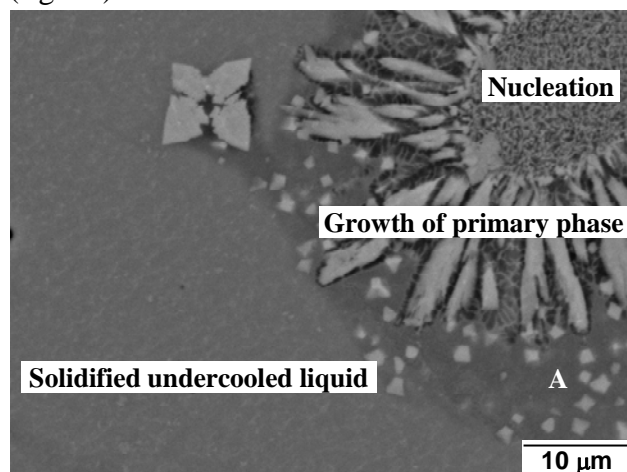


Figure 5: Various microstructural features generated after deposition and fragmentation of a partially solidified droplet.

This consisted of a large fraction of amorphous phase [Sri10]. Fig. 6c shows the evidence that undercooled and highly viscous droplets impinge and flatten on the substrate and solidify featureless. The viscous flow is readily visible. Fig. 6d depicts that a partially crystallized droplet, still with remaining undercooled liquid, impinge on an already deposited droplet. The viscous liquid flows, with increased surface area, and solidifies in amorphous or nanocrystalline state. Fig. 6e is a depiction of the layering of the viscous liquid one on the other. The flower-like feature in the middle is a manifestation of how a crystallized part fragments on deposition.

The above discussion confirms that the droplets experience two stage of cooling during spray deposition; and amorphization and/or nanocrystallization is the result of this phenomenon. The presence of higher fraction of crystalline phase in the oversprayed particles is also one of the indicators showing higher cooling rate during deposition.

5.3 Post deposition cooling

The accumulation of heat in the deposit due to the heat transfer from the spray may lead to crystallization of the amorphous phase or growth of nanocrystalline phases in the deposit. In such a case, even if the crystallization commences, temperature increase should be restricted to a minimum so as to avoid further microstructural growth. Therefore, the most important aspect of the process is the deposition of the undercooled droplets just before the onset of crystallization. This helps in minimal heat transfer from the spray to the growing deposit. As the crystallization is avoided during deposition, the reheating of the deposit due to release of latent heat does not take place. However, total heat content should be removed from the

deposit as soon as possible. The droplet sizes in the spray are statistically distributed, therefore, it is not possible to determine the exact deposition distance for each droplet.

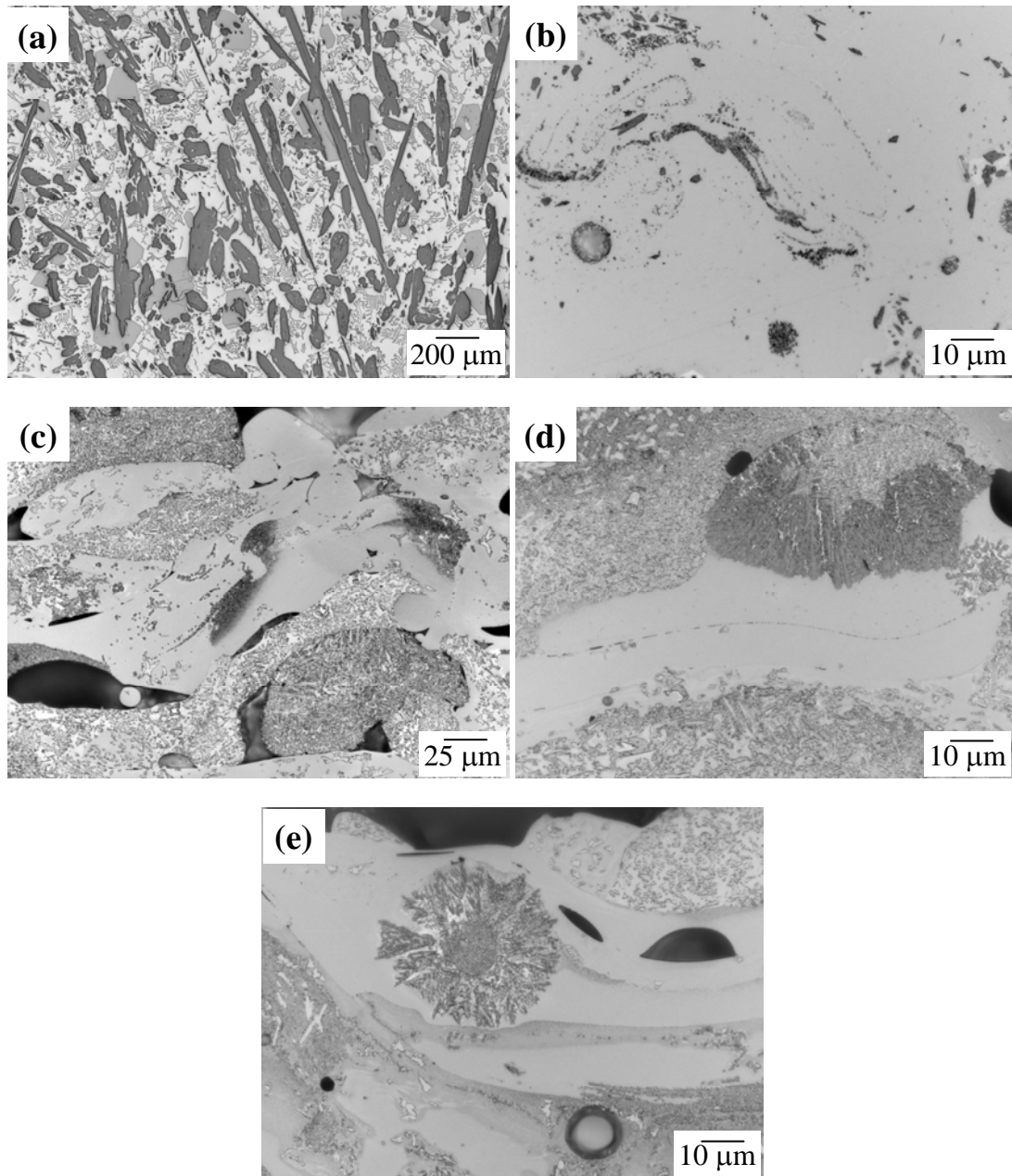


Figure 6: The deposit micrographs of $\text{Al}_{85}\text{Y}_8\text{Ni}_5\text{Co}_2$ (a to c) and $\text{Al}_{83}\text{La}_5\text{Y}_5\text{Ni}_5\text{Co}_2$ (d to e) system showing the evidence of partially crystallized particles in which the remaining liquid becomes featureless indicating amorphous or nano-crystalline structure [Sri09a, Sri10].

Therefore, to avoid any heat accumulation, which can lead to a temperature increase above the glass transition temperature, the substrate should have high conductivity as well as high heat capacity so as to affect faster heat transfer to the substrate during deposition [Sri10, Mey12]. However, it should be noted that this arrangement can be effective only up to a limited thickness; thereafter, the conduction through the deposit would be difficult due to the

amorphous nature of the deposit. Arrangements should also be in place to cool the deposit from the top surface as soon as the deposition completes.

6.0 Further prospects

The preceding discussion indicates that the development of bulk amorphous and nano-crystalline materials by spray forming has attracted considerable interest in the last 10-15 years. These were the attempts to synthesize the materials in bulk, as an alternative to other routes, and in all the cases the alloy compositions were mostly taken from those of the easy glass formers alloys i.e. Al-, Fe- and Mg-based systems. However, it seems that the understanding of the mechanism of microstructural evolution is yet to be concretized and the same need to be implemented in the process modification. This will help achieve the desired structural features. Recent results have demonstrated that the presence of nanocrystalline soft phases in an amorphous matrix gives rise to better mechanical properties as well as lead to increased toughness. This has been observed in many of the Al-based glass forming systems after crystallization from amorphous state [Ino98, Ino90, Kaw01]. In the reports from Schumacher et al. [Sch94] and Zhong et al. [Zho97] it was demonstrated that the crystallization behaviour of amorphous materials are similar to those exhibited by highly undercooled melts. These points to a possibility of synthesizing nanocrystalline composites with high strength and ductility if a process for freezing such structures are realized.

The available reports, as given in Table 1, is an indication of the emerging new horizons in the development of bulk amorphous materials by spray forming [Kim10]. It seems from various reports on the subject that the amount of amorphous phase fraction in the deposits varies irrespective of the composition. In some cases, high amorphous phase fraction could be achieved in the deposit as against that in even the small size powders [Sri10, Zhu11]. All these reports mainly emphasize the alloy composition and ensuing deposit characteristics; and there is only little effort to systematically analyse the nozzle design to achieve the desired droplet size distribution, the scale and size of deposits, cooling conditions of deposit and the process parameters. It is realized that the conventional spray forming parameters to achieve low porosity, structural refinement and homogeneity will not suffice to produce homogeneous partially amorphous or nano-crystalline materials. Fig. 7 depicts various parameters, applicable at different processing stages, to be considered for the realization of such materials in bulk. A spray formed deposit of a viscous melt is expected to engender higher porosity. However, this can be consolidated at above the glass transition temperature to achieve nano-crystalline or partially amorphous materials. If one considers the spray deposition of glass forming systems in totality, several factors would come into picture and the same is depicted in fig. 8 that summarizes the parameters such as alloy composition, purity of materials, nozzle design, substrate condition, in-flight cooling etc. needed to be considered for a successful

synthesis of nanocrystalline/amorphous materials by spray forming. The diagram lists only broad parameters and further addition of parameters are possible by carrying out more studies. In summary, the development of bulk amorphous/nanocrystalline materials is of great importance and is considered to be of high promise. The spray atomization and deposition process shows some light towards a new beginning in the synthesis of such materials. However, a good understanding of the spray forming parameters to achieve the desired properties and related modification in the process is necessary.

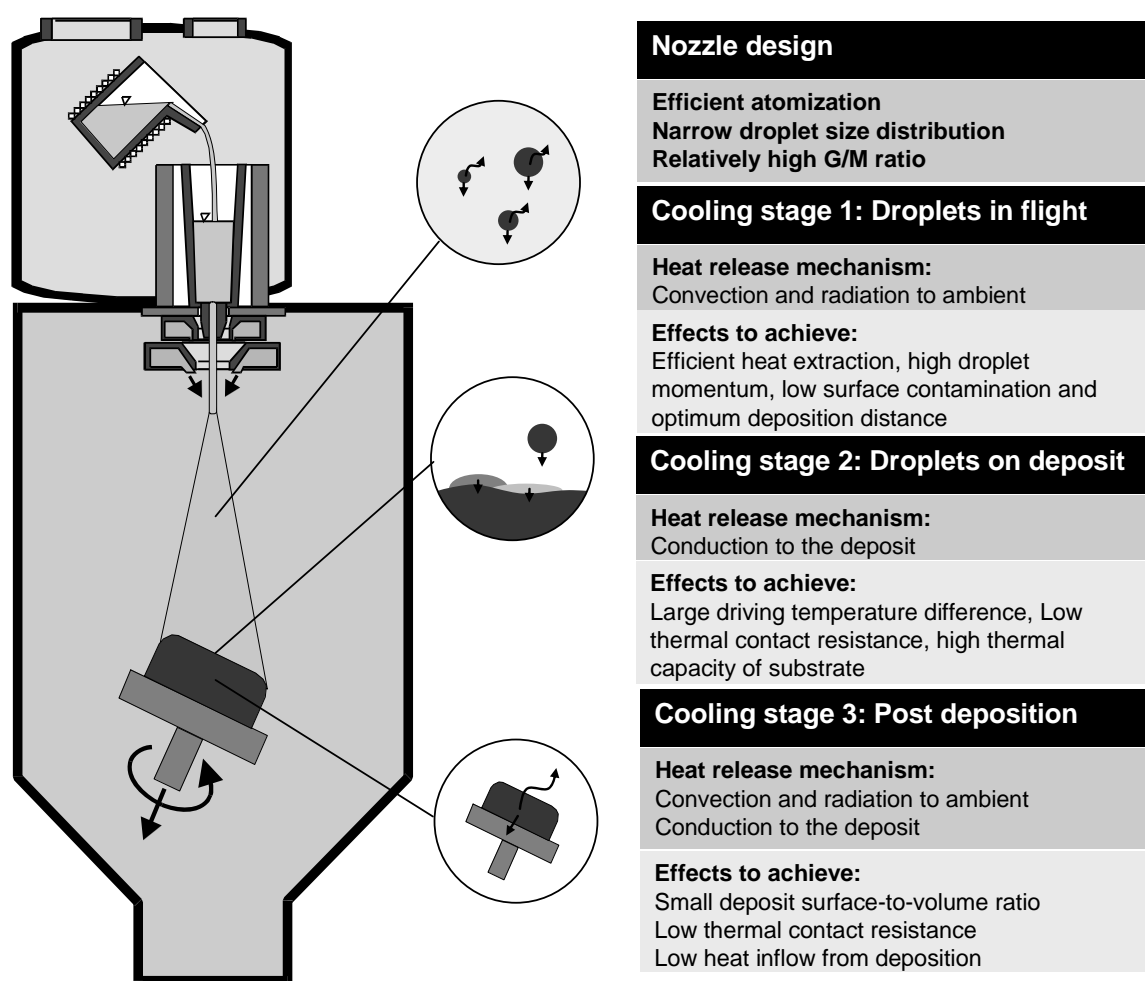


Figure 7: Process parameters to be considered at different stages of the spray deposition to achieve large fraction of amorphous/nanocrystalline structure.

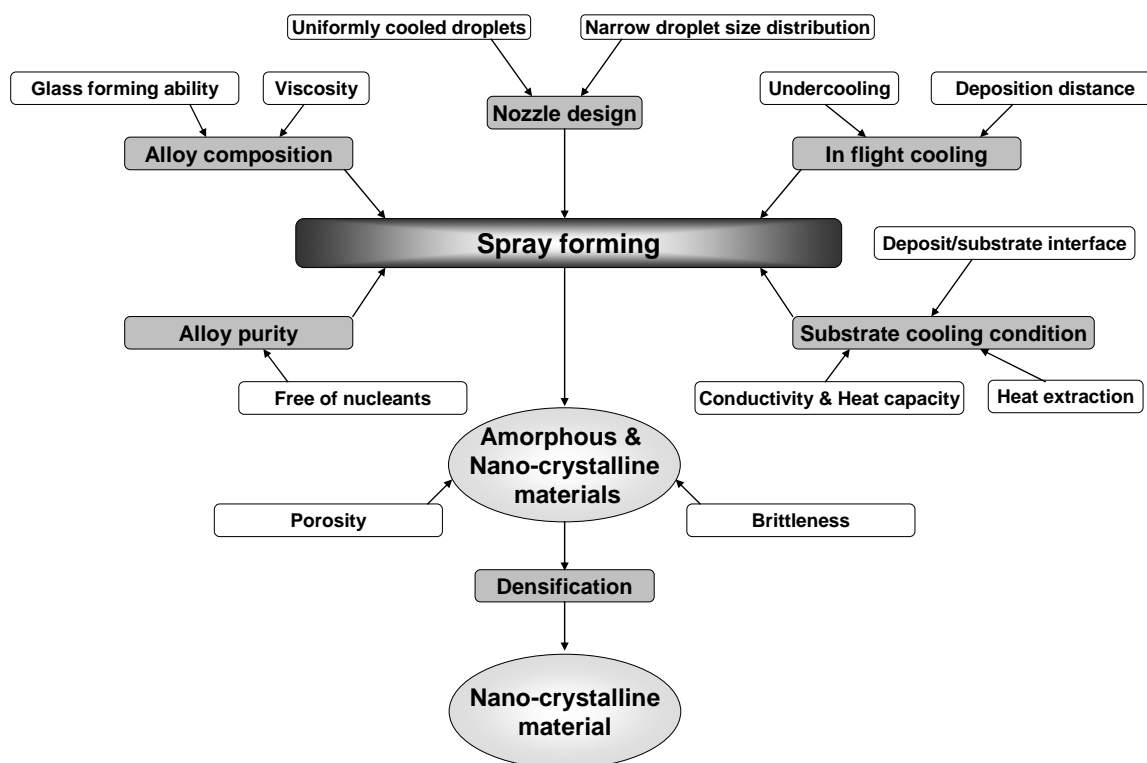


Figure 8: A schematic showing various parameters and the properties they effect during spray deposition of glass forming alloys.

7.0 Conclusions

The various aspects of bulk amorphous or nano-crystalline metallic materials development have been reviewed. The limitations of the melt spinning, melt atomization, ball milling and other techniques in the development of bulk material has been brought out. Based on the available literature from the last 20 years, it has been established that spray forming is a promising process for the synthesis of bulk amorphous/nanocrystalline materials, particularly based on the marginal glass forming compositions such as Al-, Fe, Mg- systems. However, the available reports suggest that an in depth understanding of the process, with respect to glass forming compositions, need to be developed so as to make it possible to maneuver parameters for achieving desired materials structure and properties.

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Table 1: Research reports on the spray forming of amorphous and/or nano-crystalline materials

Alloy	Thickness/amount sprayed	Amorphous fraction (%)	Characteristic phases	Year [Ref.]
Al-based systems				
Al ₈₄ Ni ₁₀ Mm ₆	7 mm	Sheet – 100%	Amorphous	1990-1991 [Ogu90, Ogu91]
Al ₈₄ Y ₃ Ni ₈ Co ₄ Zr ₁	2.1 kg	Billet- Crystallized Overspray-40%	fcc-Al, Al ₃ Zr, Al ₉ Co ₂ , Al ₁₆ Ni ₃ Y	2001 [Afo01a]
Al ₈₅ Y ₈ Ni ₅ Co ₂	7.0 kg	Billet - 76% (G/M ratio :10 m ³ /kg)	a-Al, Al ₃ Y, Al ₂ Y, Al ₉ Co ₂ , Al ₁₆ Ni ₃ Y	2001 [Afo01b]
Al ₈₉ La ₆ Ni ₅	3 mm	Sheet - 36%	fcc-Al, Al ₃ Ni, Al ₁₁ La ₃ and some unknown phases.	2005 [Guo05]
Al ₈₅ Nd ₅ Ni ₁₀	30 mm	Billet – crystalline Overspray – 63%	a-Al, Al ₆ NdNi ₂ , Al ₃ Ni, Al ₆ NdNi ₂ (secondary Crystals),	2006 [Guo06]
Al ₈₉ La ₆ Ni ₅	1-2 mm	Sheet – 36%	fcc-Al, Al ₃ Ni, Al ₁₁ La ₃	2007 [Guo07]
Al ₈₅ Y ₈ Ni ₅ Co ₂	12 mm	Bottom – 83%, Top – 56%	fcc-Al, Al ₂ Y and Al ₃ Y, Al ₂₃ Ni ₆ Y ₄	2009-2010 [Sri10, Sri1b, Kim10]
Al ₈₃ La ₅ Y ₅ Ni ₅ Co ₂	8 mm	Partially amorphous	a-Al, Al ₃ Y, Al ₁₁ La ₃ , Al ₃ Ni and unknown phases	2009 [Sri09a]
Al ₈₆ Si _{0.5} Ni _{4.06} Co _{2.94} Y ₆ La _{0.5}	12 mm	Bottom – 91.7%, Middle – 78% Top – 54.3%	fcc-Al and Al ₄ NiY	2011 [Zhu11]
Fe-based system				
Fe ₇₇ Nd ₁₅ B ₈	3 mm	Sheet – 100%	Limited Fe ₁₄ Nd ₂ B phase	1998 [Sai98]
Fe ₈₃ Zr _{3.5} Nb _{3.5} B ₉ Cu ₁	0.8 kg	Crystalline	a-Fe, Fe ₃ Nb, Fe ₂ Zr and Fe ₂ B	2004 [Afo04]
Fe ₆₃ Nb ₁₀ Al ₄ Si ₃ B ₂₀	20 mm	Bottom – 75% (up to 1 mm) Top - crystalline	a-Fe, Fe ₂₃ B ₆ , FeB and FeNbB.	2006 [Afo07]
Fe _{73.5} Cu ₁ Nb ₃ Si _{13.5} B ₉	2.2 kg	Centre – crystalline Periphery – partially amorphous	Nanocrystalline and amorphous structure	2009 [Yan09]
Fe ₆₆ B ₃₀ Nb ₄	5 mm	Periphery – 8.5% (up to 0.5 mm)	---	2010 [Bon10]
[(Fe _{0.6} Co _{0.4}) _{0.75} B _{0.2} Si _{0.05}] ₉₆ Nb ₄	16 mm	Bottom – >95% (up to 4 mm)	----	2011 [Cat11]
Mg-based and other systems				
Mg ₆₅ Cu ₂₅ Gd ₁₀	12 mm	Bottom – amorphous (0-2 mm) Middle – Partially crystalline (3-6 mm) Top - fully crystalline	---	2008 [Cha08, Cha0847,79]
La ₆₂ Al _{15.7} (Cu, Ni) _{22.3}	---	Sheet - amorphous	---	2009 [Tin09]